

# MODERN TECHNIQUES OF SURFACE SCIENCE

Second edition

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# 1

## Introduction

### 1.1 Why surfaces?

The growth in the study of solid surfaces and in the number of techniques available for their study has been enormous since the early 1960s. At least one reason for this is the growing awareness of the importance of understanding surface properties and indeed the fact that work on surfaces has had an impact on this understanding and on specific applications in the 'real world'. At a fundamental level surfaces are of great interest because they represent a rather special kind of defect in the solid state. Much of our understanding of solids is based on the fact that they are, in essence, perfectly periodic in three dimensions; the electronic and vibrational properties can be described in great detail using methods which rely on this periodicity. The introduction of a surface breaks this periodicity in one direction and can lead to structural changes as well as the introduction of localised electronic and vibrational states. Gaining a proper understanding of these effects is not only of academic interest, as there is growing interest in the properties of low-dimensional structures in semiconductor devices, and a free surface can represent the simplest case of such a structure.

Perhaps the most widely quoted motivation for modern surface studies is the goal of understanding heterogeneous catalysis. The greatly increased rates of certain chemical interactions which occur in the presence of solid (usually powder) catalyst must result from the modification of at least one of the constituent chemicals when adsorbed on the solid surface and its enhanced ability to interact with the other constituent(s) in this state. One would therefore like to understand what these modifications are, whether there are new intermediate species formed, what are the rate limiting steps and activation energies, what kind of sites on the catalyst surface are active and how these processes depend on the catalyst material.



This might lead to better or cheaper catalysts (many such catalysts being based on precious metals such as platinum). The problems of understanding these processes in a microscopic or atomistic way are formidable. Industrial processes frequently operate at high temperatures and pressures (i.e. many atmospheres) and the catalysts are in the form of highly dispersed powders (possibly with individual particles comprising only hundreds of atoms), they frequently involve transition metals on oxide 'supports' which may or may not be passive, and they may include small additions of 'promoters' which greatly enhance the efficiency of the catalysts. The approach which makes the fullest use of the techniques in this book is to study highly simplified versions of these problems. This involves initially taking flat, usually low Miller index, faces of single crystals of the material of interest and studying the adsorption or coadsorption of small quantities of atoms and molecules on them in an otherwise Ultra-High-Vacuum (UHV) environment. The stress of these methods is on characterising the surfaces and the adsorption and reaction processes in fine detail so that the conditions are very well defined. Although it is easy to see reasons why this approach may be too far removed from applied catalytic problems to be of real value, the signs in the last few years have been encouraging, and even in the early 1980s some understanding of simple catalytic reactions at a microscopic level had started to emerge from these model studies (King & Woodruff, 1982). Since then, problems of increasing complexity have been explored with significant success.

Another area of study is in the understanding of corrosion of materials and certain kinds of mechanical failure due to grain boundary embrittlement. One important process in these problems is of the segregation of minority ingredients (often impurities) in a solid to the free surface, or to internal surfaces (grain boundaries) when the temperature is high enough to allow diffusion through the bulk at a reasonable rate. A particular species can find it very energetically favourable to be in one of these surface sites rather than in the bulk so that even a bulk concentration of a few parts per million can lead to surfaces covered with a complete atomic layer of the segregant in equilibrium. Segregation of this kind is now well established as being a cause of intergranular fracture of engineering materials. On the other hand, similar segregation to free surfaces can have the effect of improving resistance to corrosion. Studies in this broadly metallurgical area have proceeded not only by the modelling type of investigation described above, but also by applying some of the techniques described in this book to the study of the surfaces of 'real' materials of

interest. In particular, by investigating the composition of the top few atomic layers of a fractured or corroded surface considerable information can be gained. To do this, one requires techniques which are highly surface specific in their analytic capabilities. Coupled with a method of removing atomic layers in a reasonably controlled fashion, usually by ion bombardment, a depth profile of the surface and subsurface composition can be obtained.

The final main area of application of surface studies which lies closest to the fundamental problems mentioned at the beginning of this section is in the fabrication of semiconductor devices. Although there are applications for depth profiling on actual devices for 'trouble-shooting' in production problems (due to contamination or interdiffusion at interfaces) there are also problems of quite fundamental importance which lie naturally quite close to the modelling approach described in relation to catalytically motivated research. For example, the formation of metal-semiconductor junctions with desirable properties is strongly influenced by the tendency for chemical interactions to occur between the metal and the semiconductor. Real devices use well-oriented single crystal samples so this aspect of the modelling is no longer idealised. Moreover, in the case of semiconductor surfaces some of the simplest problems remain far from trivial to solve. Most semiconductor surfaces appear to involve some structural rearrangement of the atoms relative to a simple extension of the bulk structure. For example, the stable structure of a Si{111} surface reconstructs to a 'superlattice' seven times larger in periodicity than the bulk (a  $(7 \times 7)$  structure in the notation described in chapter 2). A proper quantitative understanding of this complex reconstruction has proved to be one of the key problems of basic surface science, but by the late 1980s a rather clear picture had emerged using a combination of methods (of which high energy electron diffraction, a method not normally used in surface studies, and Scanning Tunnelling Microscopy (STM), played key roles). Simpler reconstructions also occur on semiconductor surfaces. Even in the case of the {110} cleavage faces of III-V compounds such as GaAs in which there is no change in two-dimensional periodicity of the surface, there is a rearrangement in bond angles influencing the relative positions of the Ga and As layers. Finally, we note that there is increasing interest in the growth of semiconductor devices by Molecular Beam Epitaxy (MBE) using methods very close to those used in surface science generally (UHV and 'adsorption' at very low rates). The surface structures formed during MBE can be very complex and highly sensitive to the stoichiometry of the uppermost layer.

Growth studies also reveal that many materials will not grow in a layer-by-layer form on certain other layers. These limitations in ‘atomic engineering’ need to be understood properly if exotic multilayer devices are to be designed and built.

This book is concerned with the analytical techniques which have contributed, and should continue to contribute, to understanding these problems. It is concerned with the basic underlying physical principles of the techniques and the extent to which those principles constrain their usefulness. As such, it is not intended to be an experimental handbook for surface analysis but the background which allows the techniques to be used and assessed properly. Some experimental details are given, but again with the primary object of understanding the strengths and limitations of individual techniques. In the final section of this chapter a very broad and brief review of the interrelationship of the main techniques is given with reference to their applications. First, however, we consider the need for UHV and define a few of the specialist terms used in surface studies.

## 1.2 Ultra-High-Vacuum (UHV), contamination and cleaning

If we are to study the properties of a surface which are well characterised at an atomic level it is clear that the composition of the surface must remain essentially constant over the duration of an experiment. This evidently means that the rate of arrival of reactive species from the surrounding gas phase should be low. A reasonable criterion would be that no more than a few per cent of an atomic layer of atoms should attach themselves to the surface from the gas phase in, say, an experimental time scale of about one hour. This requirement can be evaluated readily from simple kinetic theory of gases. Thus, the rate of arrival of atoms or molecules from a gas of number density  $n$  per unit volume and with an average velocity  $c_a$  is

$$r = \frac{1}{4}nc_a \quad (1.1)$$

while equating the kinetic energy of the particle's mass  $m$  with a root mean square velocity  $c_{\text{rms}}$  to their thermal energy determined by the absolute temperature  $T$  and Boltzmann's constant  $k_B$  gives

$$c_{\text{rms}}^2 = 3k_B T/m \quad (1.2)$$

Finally, using the relationship between the two velocities

$$c_a = (8/3\pi)^{\frac{1}{2}}c_{\text{rms}} \quad (1.3)$$

and the fact that the pressure  $P$  is given by

$$P = nk_{\text{B}}T \quad (1.4)$$

leads to an expression for the rate of arrival

$$r = P(1/2\pi k_{\text{B}}Tm)^{\frac{1}{2}} \quad (1.5)$$

A convenient form of this expression, in which  $P$  is expressed in torr (i.e. mm of Hg),  $T$  in K and  $m$  is substituted by the molecular weight  $M$  multiplied by the atomic mass unit gives

$$r = 3.51 \times 10^{22} P/(TM)^{\frac{1}{2}} \quad (1.6)$$

$r$  being in molecules  $\text{cm}^{-2} \text{s}^{-1}$ . For example,  $\text{N}_2$  molecules ( $M = 28$ ) at room temperature ( $T = 293 \text{ K}$ ) at 1 torr have an arrival rate of  $3.88 \times 10^{20}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ . It is convenient to define a monolayer adsorption time in terms of the pressure. In defining this we assume that a monolayer, i.e. a single complete atomic layer, consists of about  $10^{15}$ – $2 \times 10^{15}$  atoms  $\text{cm}^{-2}$  and that all molecules arriving at the surface stick and are incorporated into this monolayer. Thus for the example given the monolayer time is about  $3 \times 10^{-6} \text{ s}$  at 1 torr, 3 s at  $10^{-6}$  torr, or almost 1 hour at  $10^{-9}$  torr. This means that if all the gas atoms and molecules arriving at a surface in a vacuum system do indeed stick to it, then contamination of only a few per cent of a monolayer in an experimental time of 1 hour requires pressures of  $10^{-10}$  torr or better. While these are broadly worst case assumptions, some surfaces of interest do react readily with H and CO, the main ingredients of a UHV chamber and so match these conditions. The need for UHV is therefore simply to keep a surface in its clean or otherwise well-characterised condition once produced. Indeed, the need for good vacuum can also extend to the kind of depth profiling study of technical surfaces described in the previous section. In these cases a sample is initially analysed 'as loaded' so that the surface composition is dominated by contamination from handling in air and uninfluenced by the quality of the surrounding vacuum in the analysis chamber. Once surface layers have been removed in the depth profiling, however, the freshly exposed surface is susceptible to new contamination and must be studied in a good-quality vacuum.

A detailed discussion of the methods of UHV is not appropriate to this book and can be found in many volumes concerned specifically with vacuum technology (e.g. Roberts & Vanderslice, 1963; Robinson, 1968). A few points of general interest are worth noting, however. The first is

that a major reason for the development of modern surface science research in addition to those given in the previous section is the commercial availability of convenient UHV components since the early 1960s and their subsequent development. Early work was carried out in glass vacuum systems using liquid N<sub>2</sub> trapped Hg diffusion pumps. The surface science instrumentation had to be incorporated into these sealed glass vessels with electrical connections made through glass-to-metal seals in the containment vessel. Modern surface science studies usually involve the use of many different techniques in the same vessel, each of which may be quite sophisticated and this is achieved by mounting each onto a stainless steel flange which is sealed to a stainless steel chamber using Cu gasket seals. This gives great flexibility and demountability and it is hard to see how this level of sophistication could have been achieved realistically with glass systems. In addition to the development of these demountable metal vessels, great use is now made of ion pumps which require only electrical power to function and do not need liquid N<sub>2</sub> and the regular attention that this implies.

The second general point regarding UHV is the constraints on fabrication methods necessary for instrumentation within the vacuum. Although one must use vacuum pumps capable of operating in the  $10^{-10}$ – $10^{-11}$  torr range, an important ingredient in obtaining UHV is the need to ‘bake’ the whole system. In the absence of leaks and with suitable pumps, vacua are limited by the ‘outgassing’ of the inner walls and instrument surfaces within the chamber mainly due to the desorption of adsorbed gases from these surfaces. By heating all of these surfaces, the rate of desorption is increased, the surface coverage decreased, and thus the rate of desorption on subsequently cooling to room temperature is reduced. This reduces the gas load on the pumps and thus allows lower pressures to be achieved. Typically, a stainless steel chamber with all its enclosed instrumentation is baked to 200 °C for 12 hours or so. Obviously this means that all components in the vacuum chamber must be stable and have low vapour pressures at 200 °C. An additional common requirement for the experiments described in this book is that all components must be non-magnetic as many surface techniques involve low energy electrons which are easily deflected by weak electrostatic and magnetic fields. Fabrication methods compatible with these requirements are now well established involving mainly the use of stainless steel and refractory metals with ceramics for electrical or thermal insulation. Many materials acceptable in ‘high vacuum’ ( $\sim 10^{-6}$  torr) such as many adhesives and plastics are not acceptable in UHV.

While UHV guarantees that a surface should not be influenced by the arrival of ambient atoms and molecules on a time scale of the order of one hour or more, a further requirement to studies of the properties of ideal surfaces is to be able to clean them, in the vacuum system, to a level compatible with the contamination constraints we have set on the vacuum, i.e. to be able to produce a surface which contains no more than a few per cent (and preferably less) of an atomic layer of species other than those which comprise the underlying bulk solid. Generally we also require that the surface is well ordered on an atomic scale. The main methods used to achieve this *in situ* cleaning are

- (i) cleavage,
- (ii) heating,
- (iii) ion bombardment (typically Ar ions),
- (iv) chemical processing.

The first of these is largely self-explanatory; for those materials which do cleave readily (e.g. oxides, alkali halides, semiconductors, layer compounds) and for studies of the surface orientation which comprises the cleavage face, surfaces can be prepared in vacuum which are intrinsically clean. Apart from these limitations the main problem with the method is that it is usually only possible to cleave a single sample (e.g. a long bar) a few times, so that the surface cannot be reprepared many times, and that the cleavage may result in a heavily stepped surface. Large variations in the properties of a surface (particularly the adsorption kinetics) can be obtained from cleave to cleave on many materials. There are examples, moreover, of cases in which the cleavage surface presents a different structure from that obtained by heating to allow the surface to equilibrate; the Si{111} surface is an example of this.

Heating a surface, like heating the walls of a vacuum vessel, can lead to desorption of adsorbed species. However, in most cases some impurities on the surface are too strongly bound to be removed by heating to temperatures below the melting point of the sample. This method of cleaning has been most used for W and similar high melting point materials for which the surface oxides are flashed off below the melting points. Even for these materials, however, it is unlikely that the method can be totally satisfactory due to impurities such as C which form exceedingly strongly bound compounds with the substrate material. On the other hand, once these kinds of impurities have been removed, heating alone may be sufficient to regenerate a clean surface following an adsorption experiment using more weakly bound adsorbate species. This

surface regeneration by heating may be applicable to many materials for which heating alone is totally ineffective in the initial cleaning process.

The use of Ar ion bombardment of a surface to remove layers of the surface by sputtering is by far the most widely used primary method, particularly for metal surfaces. The actual physics of this process and the yields obtained are discussed in chapter 4. The technique is effective in the removal of many atomic layers of a surface and even if an impurity species is far less effectively sputtered than the substrate it can be removed eventually. One disadvantage of ion bombardment, typically at energies of 0.5–5.0 keV, is that the surface is left in a heavily damaged state, usually with embedded Ar atoms, so that the surface must be annealed to restore the order. This in itself can create problems; as was noted in the previous section, many dilute impurity species in the bulk of a solid segregate preferentially to the free surface and if a sample with a clean surface is heated, the diffusion rates are increased and further segregation can occur. Typical segregants in transition metals of very high average purity are C and S. This then requires further ion bombardment cleaning, further annealing and so on. In practice a number of cycles (possibly tens of cycles) of bombardment and annealing leads to depletion of segregating impurities in the subsurface region and to a clean surface. Far fewer cycles are then required for recleaning the sample after adsorption studies.

The final approach of chemical cleaning *in situ* involves the introduction of gases into the vacuum system at low pressures ( $\sim 10^{-6}$  torr or less) which react with impurities on a surface to produce weakly bound species which can be thermally desorbed. It is most widely used for the removal of C from refractory metals such as W which can be cleaned of most other impurities by heating alone. Exposure of such a surface to O<sub>2</sub> at elevated temperatures leads to removal of C as desorbed CO leaving an oxidised surface which can then be cleaned by heating alone.

### 1.3 Adsorption at surfaces

Although many of the techniques described in this book are applicable to a wide variety of surface problems, we concentrate the development and illustration of the techniques in terms of studies on well-characterised low index single-crystal surfaces and adsorption of atoms and molecules on them, although not all the techniques are restricted to such studies. It is therefore helpful to define some of the terms and units used in these studies which we will have cause to use in later chapters. The first of these is the definition of a *monolayer* of adsorbate. One way of defining the

Table 1.1 *Effect of 1 Langmuir exposure of different adsorbates at 300 K*

Incident and adsorbing species	No. of molecules arriving ( $\text{cm}^{-2}$ )	Coverage on Ni{100} with unity sticking factor (monolayers)
H <sub>2</sub> adsorbing as H	$1.43 \times 10^{15}$	1.80
O <sub>2</sub> adsorbing as O	$3.58 \times 10^{14}$	0.44
CO adsorbing as CO	$3.83 \times 10^{14}$	0.24
I <sub>2</sub> adsorbing as I	$1.27 \times 10^{14}$	0.16

coverage of a surface at monolayer level – i.e. of a single complete atomic or molecular layer – is in terms of the coverage of a two-dimensional close-packed layer taking account of the atomic or molecular size. Such a definition is frequently used in studies of polycrystalline surfaces. However, on surfaces of well-defined crystallography it is generally more convenient to use a definition based on the atomic density of packing of the surface itself. We shall therefore use the definition that a monolayer of adsorbed atoms or molecules involves a number density equal to that of the atoms in a single atomic layer of the substrate material parallel to the surface. In the absence of reconstruction, this is, of course, the same as the number density of atoms in the top atomic layer of the substrate. Frequently, incidentally, saturation of a particular adsorbate species occurs at a coverage of less than one monolayer so the definition implies nothing about the maximum possible coverage which depends on the adsorption system under study.

A second definition concerning adsorption studies is for a unit of exposure. The unit which is firmly established in the literature is the *Langmuir* (abbreviated as L), with  $1 \text{ L} = 10^{-6} \text{ torr s}$  exposure. A major disadvantage of this unit is that, as may be readily appreciated from equation (1.6), the actual number of atoms or molecules arriving at a surface in 1 L of exposure actually depends on the molecular weight of the gaseous species and its temperature. Table 1.1 illustrates the effect of this variation, showing the number of molecules striking  $1 \text{ cm}^2$  of surface in 1 L with a gas temperature of 300 K. Also shown here is the coverage, in monolayers, which would result if all the molecules arriving were to stick on a Ni{100} surface, with dissociation assumed for H<sub>2</sub>, O<sub>2</sub> and I<sub>2</sub>. Despite this disadvantage and the fact that the unit is certainly not an SI one, it has the great advantage of experimental convenience as most



researchers performing an exposure are equipped with an ion gauge, calibrated in torr, and a stopwatch! It provides a convenient unit for characterising the exposures needed to produce certain adsorption states on a surface and allows some transferability between experimenters working on the same adsorption system. It also is a unit of convenient magnitude in that, as table 1.1 shows, 1 L corresponds to of the order of 1 monolayer coverage if all molecules stick to the surface. Although a proposal for a unit based on the actual number of impinging molecules was made by Menzel & Fuggle (1978) it has not gained any serious support in subsequent literature. One further point which is worth mentioning in the context of table 1.1 is the question of sticking factors. The final column of table 1.1 is constructed assuming that all impinging molecules stick to the surface (i.e. that the 'sticking factor' is unity) independent of coverage. In fact this would represent a relatively unusual state of affairs. As the coverage increases, some molecules arriving at the surface will strike other adsorbed species rather than the clean surface. Assuming that these also stick (and then may diffuse over the surface to fill clean surface sites) actually involves assuming that second layer adsorption (albeit possibly more weakly bound) is possible. An alternative possibility, that the molecules arriving at occupied sites are not adsorbed, leads to an average sticking factor which falls exponentially with time. This *Langmuir adsorption* is one of several possible forms of adsorption kinetics discussed in many books on adsorption (e.g. Hayward & Trapnell, 1964) and will not be discussed further here. We should note only that in serious studies of adsorption kinetics, exposures given in Langmuirs and based on ion gauge readings of total chamber pressures are unlikely to be very reliable due to difficulties in establishing the pressure at the sample and the need for ion gauge calibration. For the same reason, exposures determined in the same way in different chambers and in different laboratories as those needed to obtain particular adsorption states may well show variations of a factor of 2 or more.

Finally, in this book we shall frequently choose examples of adsorption systems which may be referred to as involving *chemisorbed* or *physisorbed* atoms or molecules. The distinction between these two types of adsorption lies in the form of the electronic bond between the adsorbate and substrate. If an adsorbed molecule suffers significant electronic modifications relative to its state in the gas phase to form a chemical bond with the surface (covalent or ionic) it is said to be chemisorbed. If, on the other hand, it is held to the surface only by van der Waals' forces, relying on the polarisability of the otherwise undisturbed molecule, then it is said to be

physisorbed. Clearly physisorption produces weak bonds while chemisorption often produces strong bonds. It is usual to regard the upper limit of the bond strength in physisorption as around 0.6 eV per atom or molecule, or  $60 \text{ kJ mole}^{-1}$  ( $1 \text{ eV molecule}^{-1} = 96.5 \text{ kJ mole}^{-1} = 23.1 \text{ kcal mole}^{-1}$ ). Thermal energy considerations such as those discussed in chapter 5 lead to the conclusion that such weakly bonded species would be desorbed from a surface at a temperature much in excess of 200 K. Adsorbates stable on a surface above this sort of temperature are therefore almost certainly chemisorbed. However, the distinction is strictly in terms of the form of the bond, and not its energy, and there are cases in the literature in which electronic modifications characteristic of chemisorption are seen in far more weakly bound species. A low desorption temperature does not, therefore, necessarily indicate physisorption.

### 1.4 Surface analytical techniques

The rest of this book sets out the main techniques used in the investigation of the detailed properties of surfaces so that there are a limited number of generalisations which can be made regarding the selection of specific techniques and their relative strengths and weaknesses. Broadly, in investigating surfaces we are usually interested in the *structure* of a surface, its *chemical composition* and some information on the *electronic structure* which may be in the form of the chemical state of particular adsorbed atoms or molecules, or may involve a determination of the surface electronic band structure or energy density of electronic states. In addition, a few techniques are concerned with the *vibrational* properties of the surface, notably for adsorbed species including intramolecular vibrations within adsorbed molecular species, but also the surface phonon modes of clean surfaces. In the former case, at least, much of the motivation of the vibrational spectroscopy is to identify adsorbed species, or to try to understand local structure. The listing in table 1.2 of the main techniques discussed in this book, and their abbreviated forms, gives some indication of the kind of information each gives, the ticks indicating that this kind of information is actually extracted from some experiments, while the bracketed ticks indicate a potential or a minor use of the technique in a specialised form. Clearly individual techniques often provide information in more than one of the three areas and the extent of this information varies considerably.

One generalisation which can be made in the study of surfaces by these

Table 1.2 Summary of techniques and their acronyms and abbreviations

	Structure	Composition	Electronic structure or chemical state	Vibrational properties	Chapter
Low Energy Electron Diffraction (LEED)	✓			(✓)	2
Reflection High Energy Diffraction (RHEED)	✓				2
Surface X-ray Diffraction (SXRD)	✓			(✓)	2
X-ray Photoelectron Spectroscopy (XPS)	(✓)	✓	✓	(✓)	3
Surface Extended X-ray Absorption Fine Structure (SEXAFS)	✓	(✓)		(✓)	3
Photoelectron Diffraction (PhD)	✓			(✓)	3
Auger Electron Spectroscopy (AES)		✓	✓		3
Appearance Potential Spectroscopy (APS)		✓	✓		3
Ionisation Loss Spectroscopy (ILS)		✓	✓		3
Ultraviolet Photoelectron Spectroscopy (UPS)	(✓)	(✓)	✓		3
Inverse Photoemission Spectroscopy (IPES)			✓		3
Ion Neutralisation Spectroscopy (INS)			✓		4
Low Energy Ion Scattering (LEIS)	✓	✓		(✓)	4
High Energy Ion Scattering (HEIS)	✓	✓		(✓)	4
Secondary Ion Mass Spectroscopy (SIMS)		✓			4
Temperature Programmed Desorption (TPD)		✓	(✓)		5
Electron and Photon Stimulated Desorption (ESD and PSD)	✓	✓	(✓)		5
ESD Ion Angular Distributions (ESDIAD)	✓	(✓)	(✓)	(✓)	5
Atomic Force Microscopy (AFM)	✓		(✓)		6
Scanning Tunnelling Microscopy (STM)	✓		✓		6
Field Emission Microscopy (FEM)	✓		✓		6
Field Ion Microscopy (FIM)	✓		✓		7
Work function determinations			✓		8
Molecular Beam Scattering (MBS)	✓	✓			8
High Resolution Atom Scattering (HRAS)	✓			✓	8
Infrared Reflection-Absorption Spectroscopy (IRAS)	✓	✓	(✓)	✓	9
High Resolution Electron Energy Loss Spectroscopy (HREELS)	✓	✓	(✓)	✓	9